

98-334057/30
HOECHST AG

A60 E19 L03

FARH 96.12.11

DE 19651439-A1

96.12.11 96DE-1051439 (98.06.18) C07C 47/546, 17/16, 22/04,
255/33, 331/04, C08G 61/00, C09K 11/06, C07F 9/28, C07C 265/08,
47/55, 45/29

Preparation of bi:aryl derivative - by reacting two aryl derivatives to give intermediate product and reducing, selectively oxidising or exchanging with (pseudo)halogen

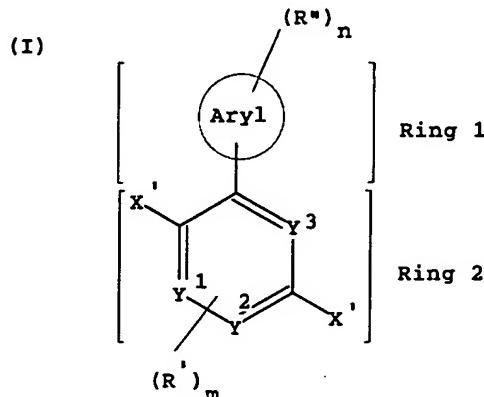
C98-103594

Addnl. Data: SPREITZER H, KREUDER W, BECKER H, KRAUSE J

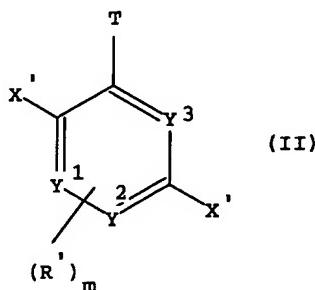
Preparation of biaryl derivative of formula (I) comprises: (A) reacting two aryl derivatives of formulae (II) and (III) in solvent in the presence of a palladium catalyst at 0-20°C to give an intermediate product of formula (IV); (B) if X' = COOR⁸ (IVa), reducing to give X = CH₂OH (IVb);

(Ca) selectively oxidising to give X = CHO or (Cb) exchanging the OH group to a (pseudo)halogen to give Z = Cl, Br, I, CN, SCN or NCO; and optionally (D) giving (I) with Z = Cl, Br, I, CN or SCN by reacting with (I)

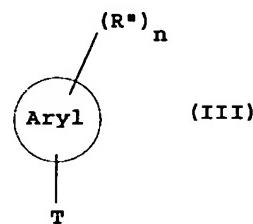
A(1-A2, 1-E, 1-E2, 1-E6, 1-E10) E(7-D, 10-A14A, 10-A15A, 10-A15E, 10-B1B, 10-D1C, 10-E4, 10-J2B3) L(3-D1, 3-H4A)



DE 19651439-A+



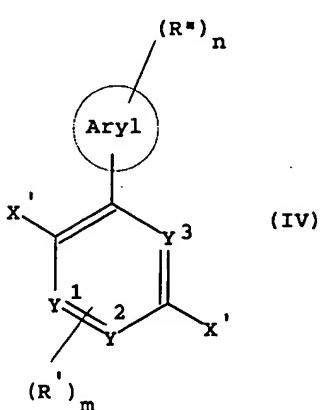
(II)



(III)

DE 19651439-A+/1

98-334057/30



(IV)

Z = PO(OR¹)₂, PO(R²)₂ or P(R³)₃⁺A⁻;
X = CH₂Z or CHO;

Y¹ - Y³ = CH or N;
Z = Cl, Br, I, CN, SCN, NCO, PO(OR¹)₂, PO(R²)₂ or P(R³)₃⁺A⁻;
Aryl = 4-14C aryl;
R', R'' = 1-20C alkyl or alkoxy where CH₂ group(s) can be substituted by O, S, CO, COO, OCO, NR⁴, (NR⁵R⁶)_a OR CONR⁷, H atom(s) can be substituted by F, CN, F, CL or 4-14C aryl optionally substituted by R';
R-R³ = 1-20C hydrocarbon;
R⁴-R⁷ = H or 1-20C hydrocarbon;
A⁻ = anion or equivalent;
m = 0-2;
n = 1-5;
X' = CH₂OH or COOR⁸;
one of T and T' = Cl, Br or I or 1-12C perfluoroalkyl sulphonyl;
the other one of T and T' = SnR₃ or BQ₁Q₂; Q₁, Q₂ = OH, 1-4C alkyl or alkoxy, phenyl optionally substituted by halogen or 1-4C alkyl or alkoxy, or halogen, or Q₁ + Q₂ = 1-4C alkylene dioxy optionally substituted by 1-4C alkyl; and
R⁸ = H or 1-12C hydrocarbon.

DE 19651439-A+/2

Also claimed are the above biaryl derivatives per se.

MORE SPECIFICALLY

Z = Cl, Br, CN, PO(OR¹)₂, PO(R²)₂ or P(R³)₃⁺A⁻, Y¹ - Y³ = CH, Aryl = phenyl, 1- or 2-naphthyl, 1-, 2- or 9-anthracenyl, 2-, 3- or 4-pyridinyl, 2-, 4- or 5-pyrimidinyl, 2-pyrazinyl, 3- or 4-pyridazinyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinoline, 2- or 3-thiophenyl, 2- or 3-pyrrolyl, 2- or 3-furanyl or 2-(13,4-oxadiazol)yl, R' = 1-12C alkoxy, R'' = 1-12C alkyl or alkoxy, m = 0 or 1 and n = 1-3.

USE

The biaryl derivatives are used in the preparation of polymers (claimed) which are useful as electroluminescence materials.

ADVANTAGE

Gives high purity.

PREFERRED PREPARATION

T = I, Br, Cl or 1-12C perfluoroalkyl sulphonate and T' = QR₁R₂, X = COOR⁸.

In step (B), the intermediate product (IV) is obtained by reaction with (I) LiAlH₄, diisobutyl aluminium hydride, THF or toluene; (ii)

borohydrides; (iii) H in the presence of a catalyst; or (iv) Na or NaH. In step (Ca), product (IVa) is obtained by oxidation with DMSO/oxalylchloride or either pyridinium chlorochromate or pyridinium chromate.

In step (Cb), product (IVb) is obtained by reacting with HCl or HBr or either thionyl chloride or thionyl bromide in a compound of formula (Ib) (I: X = Cl or Br).

In step (D), a compound of formula (Ib) is obtained by reaction with a trialkyl phosphate in a bisphosphate or formula (Ic) (I: X = PO(R¹)₂).

EXAMPLE

30.1 g 2-bromoterephthalic acid diethyl ester, 27.6 g K₂CO₃, 140 ml toluene, 26.7 g 4-hexyloxyphenyl boronic acid and 1.16 g Pd(PPh₃)₄ were reacted at 85°C under Ar, followed by work-up to give 44.7 g 2-(4'-hexyloxyphenyl) terephthalic acid diethyl ester as a yellow-brown oil of purity 85%.

40 g of the product was treated with 5.3 g LiAlH₄ in 200 ml THF, followed by work-up to give 20.3 g 2,5-bishydroxymethyl-4'-hexyloxybiphenyl as colourless needles of purity above 98% and m.pt. 72.5-74°C.

200 mmol HBr in HAc was mixed with 12.6 g of the product. Work-up

| DE 19651439-A+/3

98-334057/30

gave 16.9 g 2,5-bisbromomethyl-4'-hexyloxybiphenyl as a clear, honey coloured oil of purity above 98%.

(22pp2522DwgNo.0/3)

| DE 19651439-A/4